Resistance of alkali activated slag concretes to chloride environments

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ABSTRACT: Researchers are focusing their attention on alternative binder systems using 100% supplementary cementitious materials as it allows better control over the microstructure formation and low to moderate environmental footprint. One such system being considered is alkali activated slag concretes (AASC), made by adding alkalis such as sodium hydroxide and sodium silicate to ground granulated blast furnace slag (GGBS). Whilst they have a similar behaviour as that of traditional cement systems in terms of strength and structural behaviour, AASC are reported to exhibit superior performance in terms of abrasion,acid resistance and fire protection.
In this article, the authors investigate chloride ingress into different grades of AASC. The mix variables in AASC included water to binder, and binder to aggregate ratio, percentage of alkali and the SiO_2/Na_2O ratio (silica modulus, Ms). The first challenge was to develop mixes for different range of workability (with slump values from 40mm to 240mm) and reasonable early age and long term compressive strength. Further chloride ingress into those mixes were assessed and compared with the data from normal concretes based on literature. Findings show that compared to the PC concretes, the AAS concretes have lower rate of chloride ingress.

KEYWORDS: Alkali activated slag concretes; Cement less binders; Workability optimisation; Chloride environments; Chloride resistance

1 INTRODUCTION

Alkali Activated Materials (AAM's) have been under consideration as an alternative binder system since 1908 [1]. However, despite having been aware of this materials potential for over a century, there is still relatively little known about the durability of AAM, especially the resistance to chloride ingress. Concrete is the foundation of modern civilisation, and cement is the component that contributes the most to carbon footprint of concrete. With an increasing concern over global warming, lower carbon emission is becoming a key factor in all areas of society. AAM's in general has lower embodied carbon dioxide than cement whilst offering similar strength characteristics, and depending on the mix this can be less than half the CO_2 cement produces per ton [2] while according to MPA new CEM I emissions are 640kg/ton. The Co_2 emission of the best mix in this study has been evaluated and is 40% of the mix produced with 100% CEM I. Another factor contributing to the renewed interest is that AAM's use industrial by-products as precursor, and so the potential for reducing material going to landfill and also using up the stockpile of ash and other by-products is also appealing.
There are three main types of AAM, each based on the precursor used, Metakaolin, Pulverised Fly Ash (PFA) and Ground Granulated Blast furnace Slag (GGBS). GGBS appears to be closest to conventional cement, and does not require curing at elevated temperature. In general, GGBS based AAM requires less activator than other AAMs, to start the reaction and to form the binder [3-5]. There is limited data available on resistance to chloride ingress in AASC. However, the findings reported by Torgal et al. suggest that the steady state diffusion of chlorides in AAS binder is about $1.0x10^{-14}$ m^2/s, which is much lower than in Ordinary Portland Cement binders ($1.4x10^{-13}$ m^2/s) [6].

The workability of AASC using crushed aggregates is an area of concern as often excess water is required to enhance the workability. As the water evaporates out of the final product, larger pores are formed and this will increase the chloride ingress. Therefore, an experimental programme was developed to study the workability, strength development and resistance to chloride ingress for a range of AASC mixes. Workability ranging from S2 to S5 were (S2~40mm to S5> 220mm) were targeted by changing the water to binder ratio, binder content, percentage of alkali and the silica modulus (SiO_2/Na_2O ratio, Ms). Further the fresh properties, compressive strength at different ages, surface electrical resistivity (SR), bulk resistivity and non-steady state chloride migration were determined and reported for these various AAS concretes.

2 EXPERIMENTAL DETAIL

2.1 Materials

The primary raw material used in this study is a granulated blast furnace slag which was provided by ECOCEM - Ireland. The chemical and physical properties are presented in Table 1 and 2.

Table 1: Oxide composition of GGBS

precursor	Component (mas% as oxide)					
	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	LOI
GGBS	35.7	11.2	43.9	0.3	6.5	0.31

Table 2: Physical properties of GGBS

ECOCEM GGBS	
Fineness ≥45µ	7.74%
Particle density	2.86
Water absorption	35.14%

Sodium hydroxide (NaOH) powders (or pellets) were dissolved in water to produce the alkaline solutions. The chemical composition of the sodium silicate solution was 15.5% sodium oxide (Na_2O), 30.5% silicon oxide (SiO_2) and 54% water. In this study, NaOH% was selected 4, 6, and 8% of slag weight and silicate modulus was selected 0.45 and 1.0.

The aggregates used in this study was crushed basalts from local sources in Northern Ireland and comprised 16.5mm and 10mm crushed coarse and fine aggregates and 4mm sand. These were combined in a ratio of 48:12:40 to get the maximum packing density in AASC mixes. Properties of both the aggregates are reported in Table 3. Potable tap water (i.e. drinking quality water) was used to make the concrete mixes.

Table 3: Physical properties of aggregates

Aggregates	Bulk specific gravity	Bulk SSD Specific gravity	Water Absorption (%)
Sand(0-4mm)	2.72	2.73	0.75
Fine Crushed Agg. (5-10mm)	2.67	2.75	3.14
Coarse Crushed Agg.(10-16mm)	2.60	2.67	2.60

2.2 Mixing

All the concrete mixtures were mixed in a laboratory pan-mixer. Crushed basalts aggregates and sand were dry mixed together for a minute and after adding the GGBS powder, mixing continued for 2 minutes and then the sodium hydroxide solution was added and after 2 minute further mixing, sodium silicate solution was added and mixing continued for a minute. The details of the different mixtures and their essential properties are presented in Table 4.

2.3 Measuring fresh properties

The slump test and flow test of each mix was carried out and the air content of mixes was measured in accordance with BS EN 12350 [7-8].

2.4 Casting and curing of the specimens

From each concrete mix, nine 100x100mm cubes, three 100x200mm cylinders and one 250x250x150 mm block were cast for the determination of compressive strength[9], 4-point Wenner probe electrical resistivity, bulk resistivity and chloride diffusivity[10]. The concrete specimens were cast in three layers and compacted on vibrating table. After casting, all the moulded specimens were covered with plastic sheets and left in the casting room for 24h. They were then demoulded and the block was wrapped in three layers of plastic wrap and other samples kept in a sealed plastic zip bag until test date.

2.5 Test preparations and procedures

In order to determine chloride diffusivity of AAS concretes three cores of diameter 100 mm per mix were cored from the 250x250x150 mm concrete block at age of 42 days. A slice with a thickness of 50 mm was cut off from each core after removing 5mm from top finishing surface. The vacuum saturation regime was used to precondition the slices so that the chloride flow is predominantly diffusive and initial sorption or capillary forces do not dominate. The vacuum was applied to remove air for three hours duration and released afterwards. Samples were wrapped in hessian saturated in deionised water to prevent leaching of ions from them and placed in the container. The weight of the sample was noted after an hour for weight (W1) and then apply vacuum followed by further saturation. Weight was checked again (W2). Usually after 6 hour, when W_i-$W_{(i-1)}$ was less than 0.1%, i.e., <1g of change for a 1kg, the samples were considered fully saturated. After conditioning to a surface-dry condition, an epoxy resin (Sika Gard-680S) was applied onto the surfaces of the specimens in three layers except the two test surfaces (cut surface). Chloride penetration depth and non-steady state migration coefficient of these concretes were determined by carrying out the test as outlined by NT BUILD 492 [10].

Figure 1 Cells for performing non-steady state migration test as per NT Build 492 [10].

Bulk resistivity measurement was performed on the same samples before and after the NT BUILD 492 test. Test set-up for measuring resistivity is shown in Figure 2.

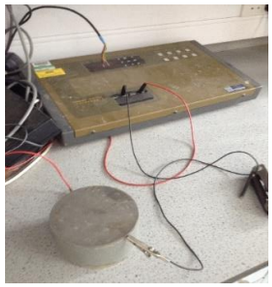

Figure 2 Bulk resistivity test equipment and sample

The surface resistivity was determined using the Wenner four-probe on 100x200mm cylinders. The top face of cylinder was marked at the 0, 90, 180, and 270 degree points and four-probe SR meter was placed on the longitudinal surface of the concrete ensuring that all four probes were in contact with the concrete surface at each degree, see Figure 3. The resistivity measurement was recorded (two values at each degree) and the average of eight measurements was taken as the surface resistivity.

Figure 3 Surface resistivity test equipment and samples

3 RESULTS AND DISCUSSIONS

3.1 Fresh properties and compressive strength

The slump value of the concretes show that all the mixes had a slump greater than 40 mm. The mix design for the AAS concretes consisted of using various water to binder ratio, binder content, percentage of alkali and the SiO_2/Na_2O ratio (silica modulus, Ms) to get different grade of AAS concretes with different classes of workability (Table 4).

Table 4: The details of the different mixtures and their properties

Mix No.	Slag (kg/m3)	Ms (=SiO_2/Na_2O)	NaOH (%)	W/B	Slump (mm)	2days Comp. St. (MPa)	28days Comp. St. (MPa)	Concrete Grades
1	300	0.45	4	0.6	40	15.3	27.1	M25
2	360	0.45	4	0.7	225	11.1	21.5	M20
3	400	0.45	4	0.6	215	15.3	26.4	M25
4	400	0.45	4	0.55	108	17.8	30.0	M30
5	400	0.45	6	0.6	215	21.2	35.8	M35
6	400	0.45	6	0.55	135	24.7	44.0	M40
7	400	0.45	8	0.55	225	38.4	53.6	M50
8	400	1.0	4	0.55	160	25.8	47.8	M45
9	400	1.0	6	0.55	203	33.9	62.7	M60
10	400	1.0	8	0.55	240	33.7	64.4	M60

In all the mixes, the W/B (given in Table 4) included the total water in the mix including the water from water glass. All mixes met the minimum slump and compressive strength requirement for their use in chloride environments, such as S2 and C20/25 specified in BS8500-1:2015 for XS (marine) environments. However, mixes 1 to 3 and 5 do not meet the maximum water-cement ratio stipulated by the standard. The mixes with 300 Kg/m^3 and 400 Kg/m^3 were used to study the effect of binder content on properties investigated. 300 Kg/m^3 cement content was in accordance with binder contents suggested by BS8500-1:2015 [11] for XD1 (other than sea water) environments. Comparing mix 1 and 3 shows that increasing the binder content increases the paste which is helpful in increasing the workability from 40mm to 215mm. It also decreased the air content in fresh concrete from 2.5% to 0.4% however it had no major effect on strength. This is to be expected as the mix design was done based on a particle packing optimisation and therefore, the paste is filling in the voids and strength might have been optimised by the aggregate fraction and paste strength. Thus the strength of mixes with same chemical activators contents and different slag contents does not show significant differences. Increasing 10% water doubled the workability (comparing mix 4 to mix 3), while decreasing the strength by 14%.

Literature shows that increasing the sodium oxide content results in increased workability, reduced setting times and higher compressive strength. But high concentrations resulted in loose structure in sodium hydroxide activated samples [12-15]. The slump and flow results of the concretes are presented in Figure 4 and 5. Except mix no 7, all mixes flow value follow the same trend as Slump results. For the same water to binder ratio (0.55), comparing mix no. 4, 6 and 7 and mix no. 8, 9 and 10 with two different Ms ratio shows that the slump values of the AAS concretes with same Ms ratio increased with the increase of NaOH%. While the flow values decreases in the first group with lower Ms ratio and increases in the second group with higher Ms ratio. The slump and flow values also increased with the increase of Ms which can be seen by comparing mix no. 4 to 8, 6 to 9 and 7 to 10 in three different groups with three different NaOH%. In lower NaOH%, with the increase of Ms, the increase of slump is more pronounced. An increase in modulus Ms for mixes with higher alkali content, means more silicates are present, this whilst increasing the viscosity will reduce slump.

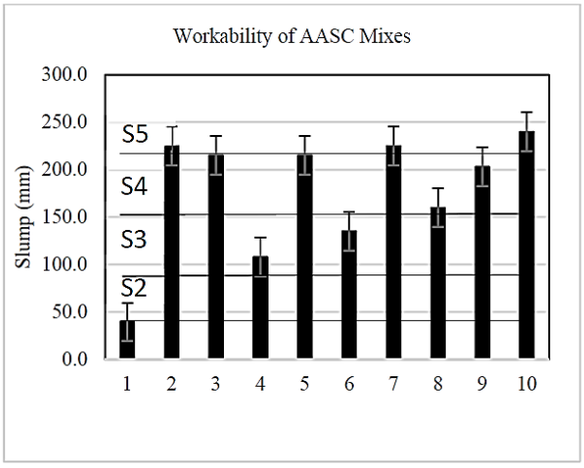

Figure 4 Slump results of AAS concretes

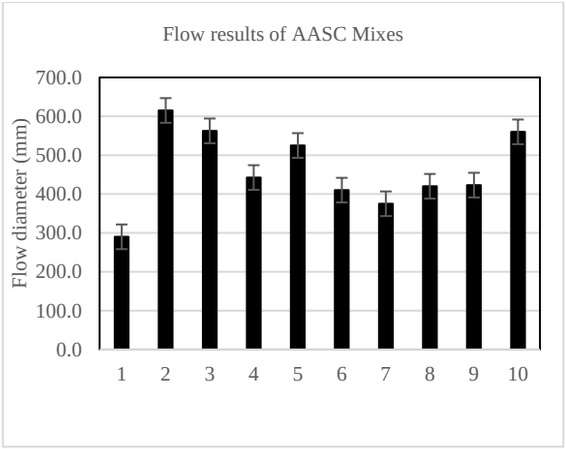

Figure 5 Flow results of AAS concretes

The air content of fresh mixes of AAS concretes is presented in Figure 6. It can be seen that in mixes made with higher alkaline percentage the air content is lower (comparing mix no. 4 to 6 and 7 and mix no. 8 to 9 and 10) and using higher silica content has had no major effect especially for mixes with lower alkaline content (comparing mix no. 4 to 8).

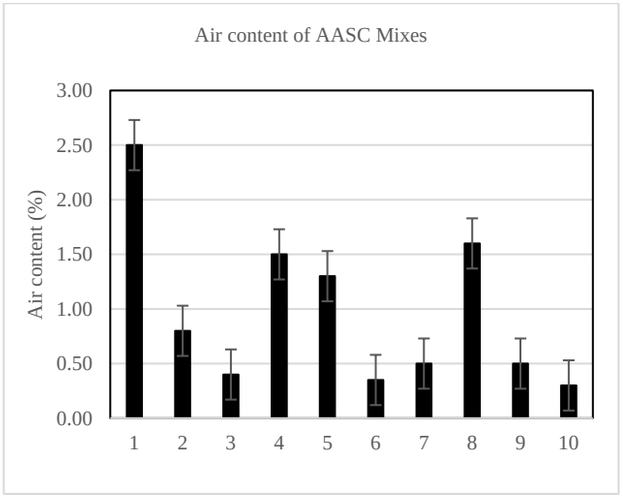

Figure 6 Air content in fresh mixes of AAS concretes

Figure 7 shows the compressive strength of AAS concretes mixes at 2, 7 and 28days. The increase of NaOH% and Ms generally increases the compressive strength of AAS concretes, which is in agreement with the results reported by the others. This can be because of more N-A-S-H (sodium alminosilicate hydrate) reacted product generated based on the increase of NaOH% and more C-A-S-H (calcium alminosilicate hydrate) reacted product produced based on the increase of SiO_2 content. From the 28 day compressive strength (Table 4) it can be seen that mix no. 9 and 10 achieved the required strength for the exposure classes XS3, XD3. It is worth noting that for mix 10 setting time was arround half an hour. Mixes no. 6, 7 and 8 seems to met the strength requirement for the exposure classes XS1, XD1 and XD2.

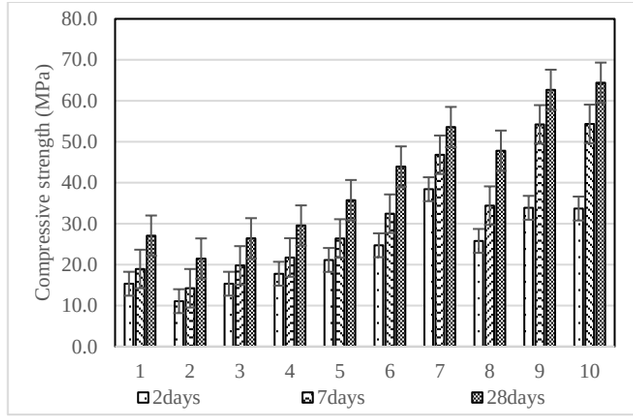

Figure 7 Compressive strength of AAS concretes mixes at 2, 7 and 28days

3.2 Resistivity and Diffusivity

Figure 8 depicts the bulk/ surface electrical resistivity for different AAS concrete mixtures, respectively. Average values of bulk and surface resistivity data (from the three replicates) for all mixtures show the resistance to flow. Therefore higher resistivity could be attributed to denser structure with low connected porosity and/or less conductivity of the binder matrix and such mixes will expected to be superior in resisting ionic (chloride) flow. They show that higher binder content in AAS concretes resulted in higher bulk resistivity but no such effect is visible on surface resistivity, indicating the lack of sensitivity of surface resistivity for assessing the whole concrete. While higher water to binder ratio (~10%) shows higher surface resistivity with no changes in bulk resistivity. Furthermore bulk electrical resistivity decreases for mixes made with higher silica modulus but surface electrical resistivity increases. This can show inhomogeneity of AAS concretes in conducting electricity from the surface layers and cross section. For mixes with same silica modulus, the surface resistivity decreases with increasing of sodium oxide percentage which is more regular in mixes with Ms=1. Whereas the bulk resistivity seems to have an extrema point which is at NaOH=6%. This may be related to the alkali content which is required to produce maximum reacted products.

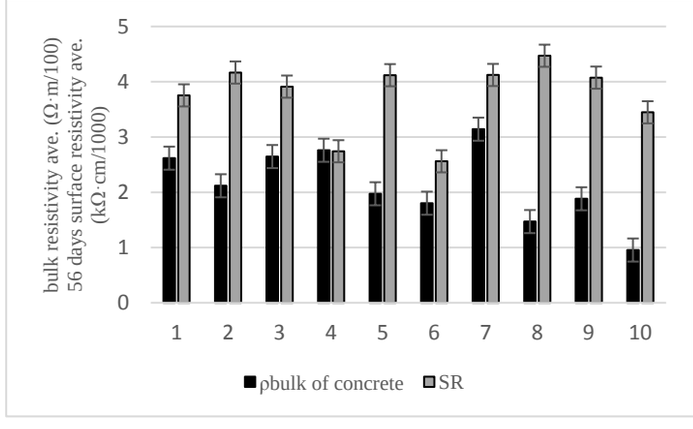

Figure 8 ρbulk and SR of the AAS concrete mixes

Figure 9 shows the bulk resistivity before and after the samples for each mix underwent chloride penetration from NT BUILD 492. These results show that the resistivity after this test is relatively close to the resistance before, and it would seem this means that the voltage used in this test does not cause damage to the specimens, and therefore influence the results. Damage to the samples from high voltage tests has been of concern with other accelerated tests [1]. More importantly, the test seems to have not altered the ionic nature of the sample and therefore the chloride penetration will be marginal as shown in Figure 11.

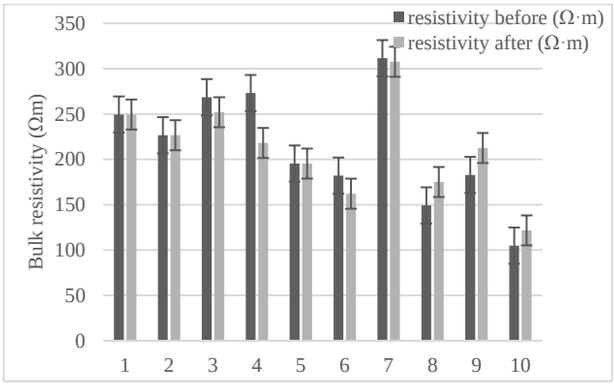

Figure 9 Bulk resistivity before and after NT BUILD 492

3.3 Chloride penetration depth

The Chloride penetration depths of samples were measured by caliper based on colour change boundary resulted after splitting the NT 492 test samples and spraying with $AgNo_3$ which is shown in Figure 10.

Figure 10 Splitted sample slices sprayed with Silver Nitrate

Figure 11 presents the chloride penetration depth in AAS concrete mixes and their non-steady state chloride migration coefficient calculated based on the penetration depth. The test voltage was considered to meet the maximum current limits in the standard between 20V and 35V and the test duration was 48hours for all the mixes which is twice of the duration suggested in standard for normal concretes. Although the pore solution conductivity of AAS concrete is higher than normal concrete, the final current passed through samples was between 10 and 30mA for different mixes which was still smaller than that passed through OPC concrete (~50mA for 30V[16]) and confirms the superior pore structure of this type of concrete. As shown in Figure 11, the chloride penetration depth of AAS concretes was between 6mm to 10.5mm for different mixes and the non-steady state migration coefficient for these concretes varried from 1.12 to $2.61*10^{-12}m^2/s$ (except mix 10 which was $3.4*10^{-12}m^2/s$). These are much lower than the depth and Dnssm reported for OPC concrete [16-17] (the chloride penetration depth of OPC concrete sample was 41.5mm and the non-steady state migration coefficient was $3.36*10^{-12}m^2/s$ for the same test voltage and half test duration).

The above non-steady state migration coefficients were calculated using the chloride ion concentration, Cd, provided in the standard. The value, 0.07N, is the chloride concentration at which the the silver nitrate produces a white precipitate. This value is for OPC concretes, and would not necessarily apply to the binders used in this study, however other research has shown that this figure is acceptable, and possibly even more accurate for binders such as GGBS [18-19]. This would indicate that the test is suitable for AAS, but to get a representative chloride depth, a higher voltage or longer duration is necessary as stated elsewhere [16].

The non-steady state migration coefficient, Dnssm, of the AAS concretes was found to be influenced by both NaOH% and Ms. For Ms equal to 0.45, an increase in NaOH% from 4 to 8 resulted in a decrease in Dnssm while the lowest Dnssm resulted when NaOH% is 8%. Ms of 0.45 and NaOH% of 8%, proved to be the optimum to give the lowest Dnssm.

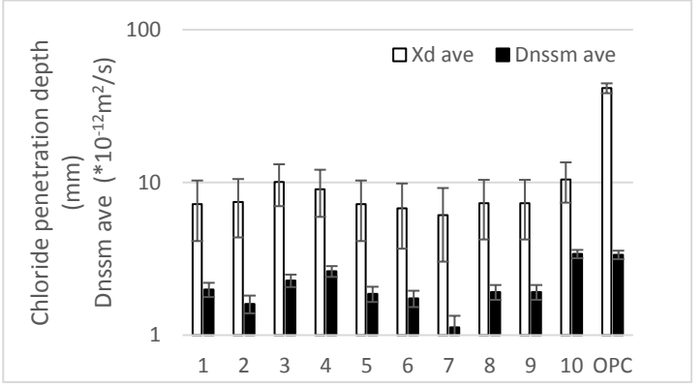

Figure 11 Chloride penetration depth and Dnssm of the ASSC mixes resulted from non-steady state chloride migration test

3.4 Correlation chloride migration coefficient and electrical resistivity

The results show that chloride ingress in AAS concretes can hardly be predicted by electrical resistivity because the resistivity of these concretes relies on pore structure and pore solution conductivity. It can be found that the non-steady state migration coefficient, Dnssm, of the AAS concretes is more related to their bulk resistivity as shown in Figure 12.

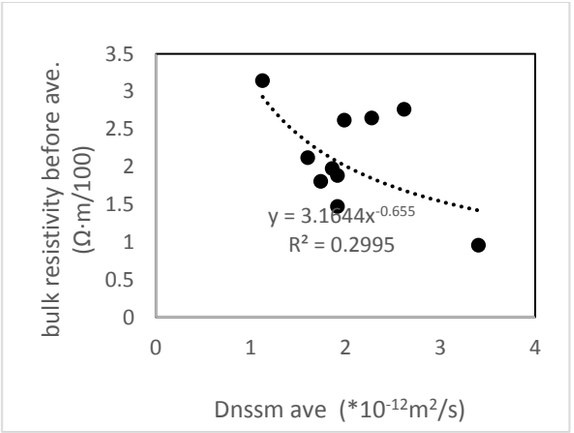

Figure 12 Correlation of Dnssm and bulk resistivity of AASC

4 Conclusion

- The work shows that AAS concretes can be designed for different class of workability and grades of concrete which are suiltable for chloride environment.
- Typically AAS concretes require a water/binder ratio of 0.55, which is close to the maximum acceptable limit, and is the limit for XD3 and XS3 chloride exposure classes.
- A modulus, Ms of 0.45 and NaOH% of 8%, proved to be the optimum to give the lowest Dnssm and minimum chloride penetration depth.
- The chloride penetration depth and the non-steady state migration coefficient of AAS concretes are much more lower than OPC concretes and comparable to PC blended concretes.

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